Electronic Supplemental Information

Selective Synthesis of Rh_5 Carbonyl Clusters within a Polyamine Dendrimer for Chemoselective Reduction of Nitro Aromatics

Zen Maeno,[a] Takato Mitsudome,[a] Tomoo Mizugaki,[a] Koichiro Jitsukawa[a]
and Kiyotomi Kaneda*[ab]

[a] *Department of Materials Engineering Science, Graduate School of Engineering Science,*
Osaka University, 1-3, Machikaneyama, Toyonaka, Osaka 560-8531, Japan

[b] *Research Center for Solar Energy Chemistry, Osaka University*

Materials and methods

All solvents and reagents were purified before use using standard procedures. Third-generation poly(propylene imine) dendrimer (**G_3**) was purchased from SyMO-Chem B.V. (The Netherlands) and dried under high vacuum before use. The PPI dendrimers were alkylated with alkanoic acid chlorides to yield **G_3-C_{16}** and **G_3-C_5**.[1S] The $Rh_6(CO)_{16}$[2S] and $[PPN][Rh_5(CO)_{15}]$[3S] were synthesized according to previously reported procedures. GC analysis was performed using a Shimadzu GC-1700 instrument equipped with an FID detector and a 30-m capillary column (Inertcap 17). The ^1H and ^{13}C NMR spectra were obtained using Jeol JNM-AL400 and Agilent 600VNS instruments. Infrared spectra were obtained using ReactIR 1000 and Jasco FTIR-4100 spectrometers. Dynamic light scattering was measured using a Horiba LB-500 instrument. The ESI-MS measurements were obtained using a Shimadzu LCMS-2010 EV instrument. The Rh carbonyl cluster solution was injected into the mass spectrometer through a syringe pump at a flow rate of 10 $\mu L s^{-1}$. Spectra were obtained in the negative-ion mode.

Synthesis of G_3-NMe_2

G_3-NMe_2 was synthesized using a procedure similar to a previously reported method.[4S] The **G_3** PPI dendrimer (9 g) was dissolved in a mixture of formic acid (100 mL) and formaldehyde (70 mL, 37%). The resulting solution was stirred for three days at 100°C, followed by concentration under reduced pressure at 65°C. Fresh formic acid (100 mL) and formaldehyde (70 mL) then were added and the mixture was refluxed for 24 h, a procedure that was repeated twice. The reaction mixture was concentrated after treatment with conc. HCl (100 mL, 37%), and NaOH (300 mL, 10%) was added followed by extraction of the alkaline mixture several times with Et_2O. After drying over $MgSO_4$, the organic layer was concentrated under vacuum. Yield: 8.2 g (90%) as a colorless viscous oil. ^1H NMR: δ = 1.38 (br, 4H, $NCH_2CH_2CH_2CH_2N$), 1.58 (m, 56H, $NCH_2CH_2CH_2N$ + $NCH_2CH_2CH_2NMe_2$), 2.20-2.40 (m, 212H, $NCH_2CH_2CH_2CH_2N$ + $NCH_2CH_2CH_2N$ + $NCH_2CH_2CH_2N(CH_3)_2$), ^{13}C NMR: δ = 24.9, 25.6, 52.3, 52.6, 56.0, 58.0.

Infrared spectra

In situ IR spectra in the carbonyl stretching region were obtained using a ReactIR 1000 instrument (ASI Applied Systems Inc.) equipped with zirconium probe in a stainless steel autoclave. Assignments were established by comparing IR data of previous reports.[5S]

Chemoselective reduction of aromatic nitro compounds

A typical procedure for the catalytic reduction of nitro aromatics was as follows. A stainless autoclave equipped with a Teflon® vessel containing $Rh_6(CO)_{16}$ (0.010 mmol), $\mathbf{G_3\text{-}C_{16}}$ (0.012 mmol), *o*-nitrobenzaldehyde (**1**) (1.0 mmol), toluene (2.0 mL), and H_2O (0.72 mL) was flushed with CO four times. The reaction mixture was stirred at 358 K under 10 atm CO. After the reaction, naphthalene (an internal standard) and THF (12 mL) was added. Conversion of the substrate and product yields were determined by GC using an internal standard method.

Gram-scale reactions of G_3-C_{16}-$Rh_5(CO)_{15}$-catalyzed chemoselective reduction of aromatic nitro compounds

A stainless autoclave equipped with a Teflon® vessel containing $Rh_6(CO)_{16}$ (0.040 mmol), $\mathbf{G_3\text{-}C_{16}}$ (0.048 mmol), 1.0 g of **1** (6.6 mmol), toluene (8.0 mL), and H_2O (0.4 mL) was flushed with CO four times. The reaction mixture was stirred at 358 K under 10 atm CO for 12 h. After the reaction, the organic phase was separated and concentrated, and then Et_2O (50 mL) was added to precipitate the dendrimer catalyst. The obtained solution was concentrated, and passed through a silica gel column (Wakogel C-200, eluent: EtOAc/hexane (1:6)). Evaporation of the solvent gave *o*-aminobenzaldehyde in 96% isolated yield (0.77 g, 6.4 mmol, mp: 39-40 ^{o}C). In the case of 2'-nitroacetophenone, 1.0 g of 2'-nitroacetphenone (6.1 mmol) gave 0.78 g of 2'-aminoacetophenone (95% isolated yield, 5.8 mmol) for 24 h.

Identification of products

The products were determined by GC-MS, GC and NMR. Retention times (GC) and chemical shifts (^{1}H and ^{13}C NMR) of the products were in agreement with those of authentic samples (commercially available) and/or reported data, as summarized below.

- 2-aminobenzaldehyde (CAS. No. 529-23-7) (Ref. 6S)
- 2-aminobenzyl alcohol (CAS. No. 5344-90-1) (Ref. 7S)
- anthranil (CAS. No. 271-58-9) (Ref. 8S)
- 2'-aminoacetophenone (CAS No. 551-93-9) (Ref. 9S)
- methyl anthranilate (CAS No. 134-20-3) (Ref. 9S)
- 2-aminobenzamide (CAS No. 28144-70-9) (Ref. 10S)
- 2-aminobenzenesulfonamide (CAS No. 3306-62-5) (Ref. 11S)
- *o*-toluidine (CAS No. 95-53-4) (Ref. 9S)
- 4-chloroaniline (CAS No. 106-47-8) (Ref. 9S)
- 4-bromoaniline (CAS No. 106-40-1) (Ref. 9S)
- *p*-aminobenzonitrile (CAS No. 873-74-5) (Ref. 9S)
- *m*-anisidine (CAS No. 536-90-3) (Ref. 9S)
- 3-aminostyrene (CAS No. 15411-43-5) (Ref. 12S)
- indole (CAS No. 120-72-9) (Ref. 9S)

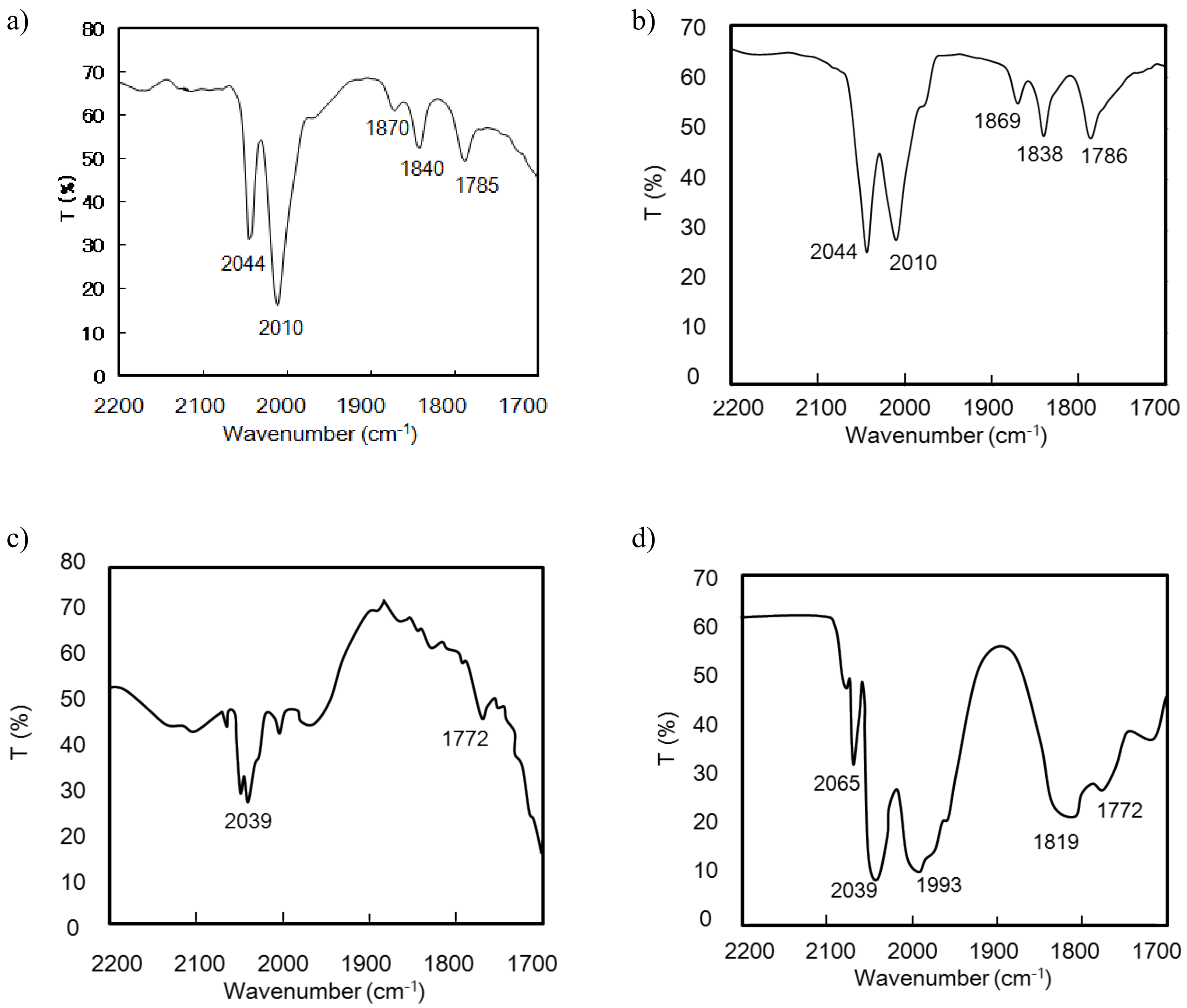


Fig. S1. IR spectra of a) **G_3-C_{16}**-$Rh_5(CO)_{15}$ under the reaction conditions; b) THF solution of [PPN][$Rh_5(CO)_{15}$] at room temperature; c) mixture of **G_3-C_5** and $Rh_6(CO)_{16}$ after treatment (toluene/H_2O, CO (10 atm), 80 °C) ; and d) mixture of **G_3-NMe_2** and $Rh_6(CO)_{16}$ after treatment (toluene/H_2O, CO (10 atm), 80 °C).

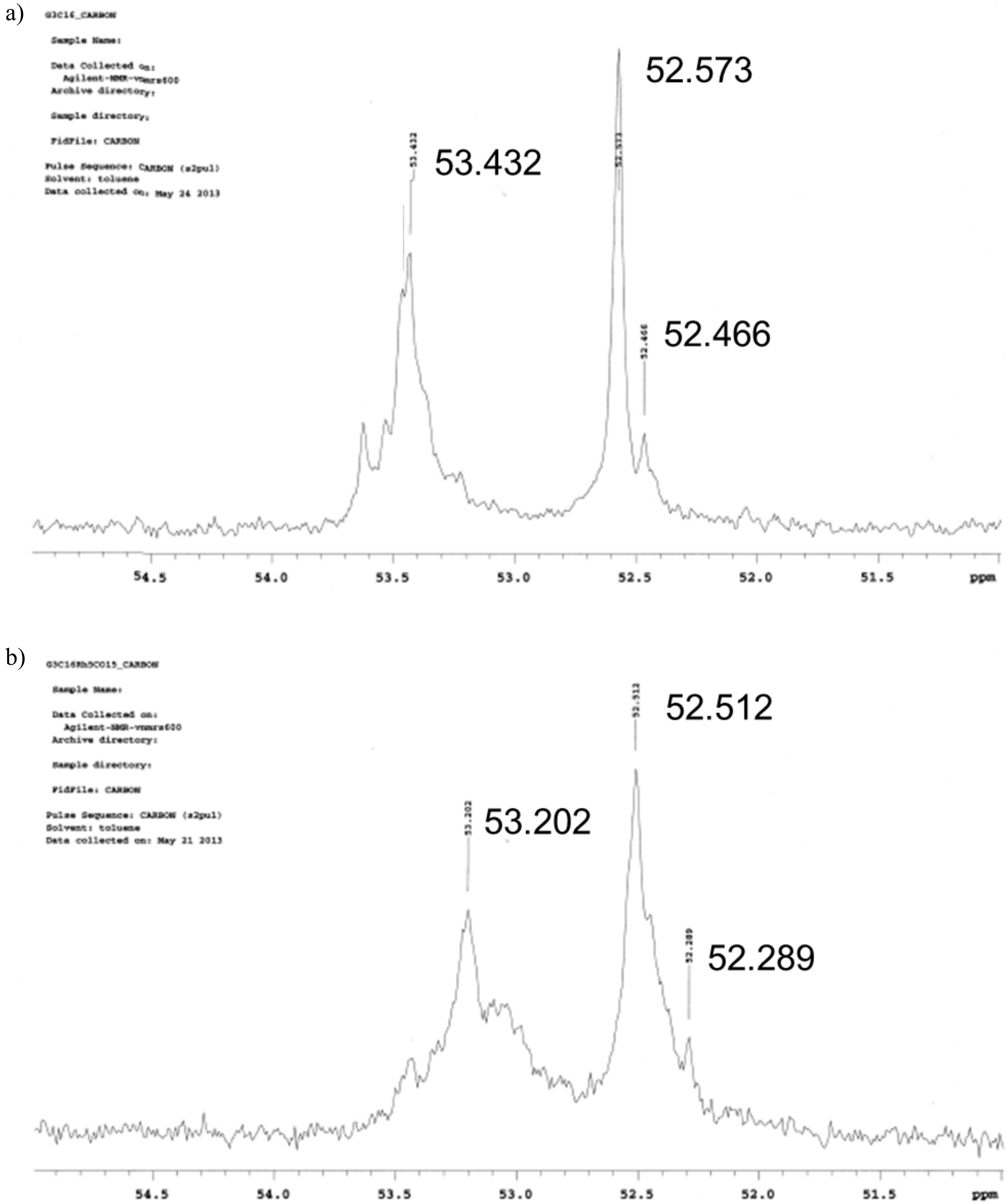


Fig. S2. ^{13}C NMR spectra in toluene-d_8 of a) **G_3-C_{16}** and b) **G_3-C_{16}**-$Rh_5(CO)_{15}$. Measurements were conducted at 80°C and under a CO atmosphere. Signals at 53.4 and 52.6 ppm correspond to α-carbons of inner tertiary amino groups (core and first generation) and outermost tertiary amino groups (second generation), respectively.

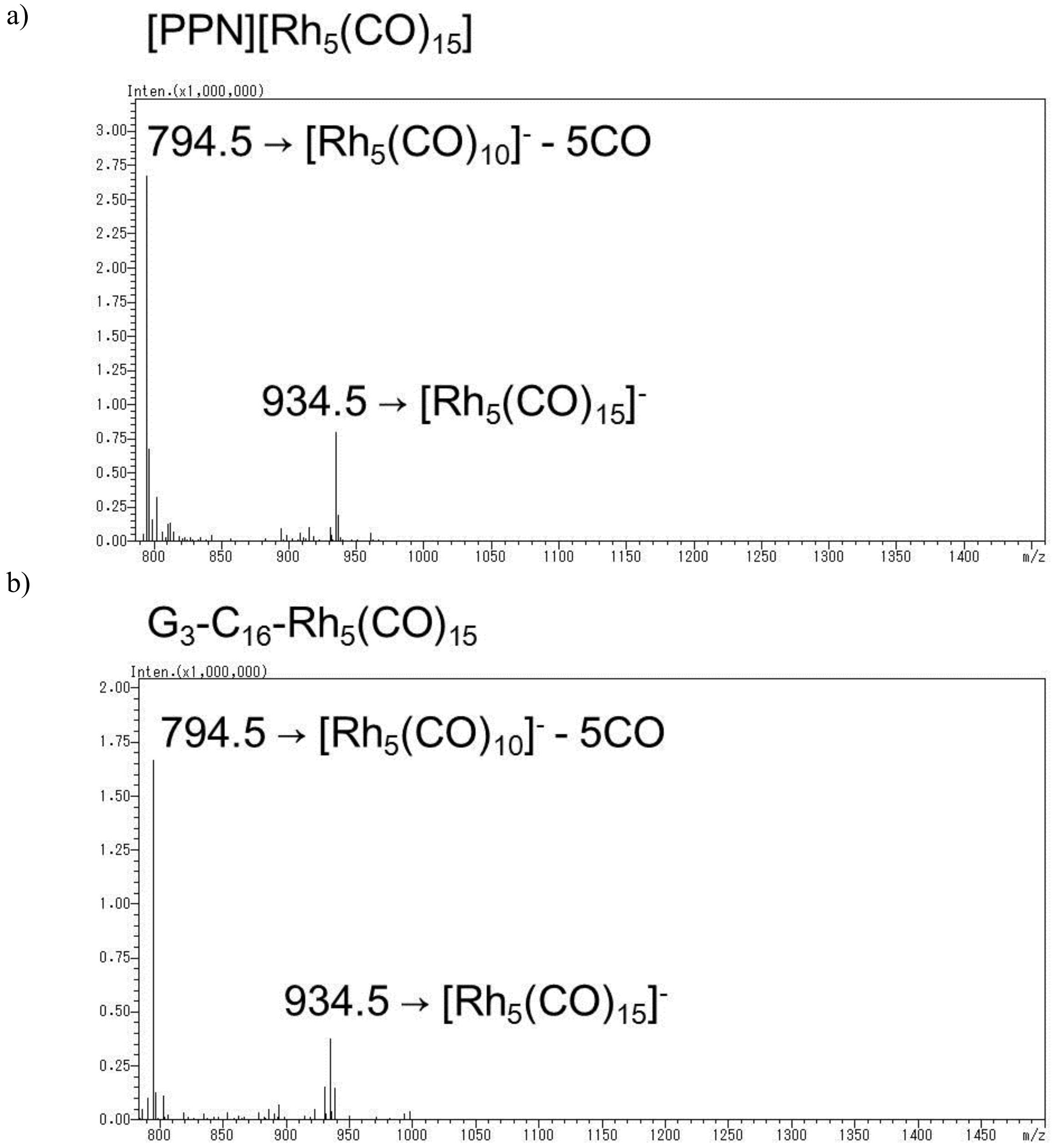
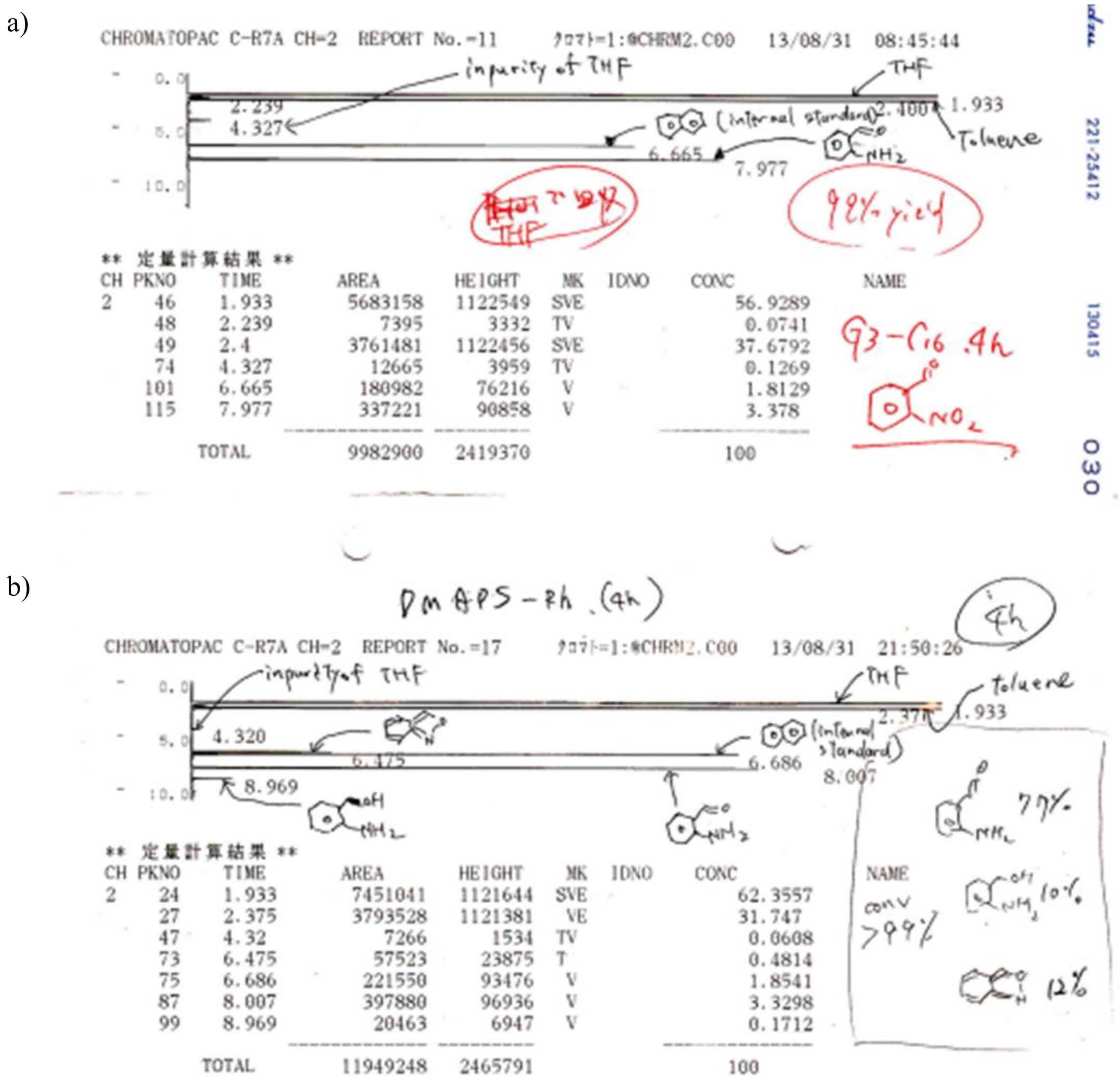


Fig. S3. Negative-mode ESI-MS spectra of the Rh carbonyl cluster a) $[PPN][Rh_5(CO)_{15}]$ (as reference) and b) fresh $\mathbf{G_3}$-$\mathbf{C_{16}}$-$Rh_5(CO)_{15}$. Spectra were obtained in solution containing the clusters (THF/water = 2/0.72).



```
CHROMATOPAC C-R7A CH=2  REPORT No.=11     ｸﾛﾏﾄｸﾞﾗﾑ=1:@CHRM2.C00    13/08/31  08:45:44

** 定量計算結果 **
CH PKNO    TIME        AREA     HEIGHT   MK  IDNO      CONC           NAME
2    46    1.933     5683158   1122549   SVE            56.9289
     48    2.239        7395      3332   TV              0.0741
     49    2.4       3761481   1122456   SVE            37.6792
     74    4.327       12665      3959   TV              0.1269
    101    6.665      180982     76216   V               1.8129
    115    7.977      337221     90858   V               3.378
                   ----------  ---------           ------------
          TOTAL      9982900   2419370                 100
```

```
CHROMATOPAC C-R7A CH=2  REPORT No.=17     ｸﾛﾏﾄｸﾞﾗﾑ=1:*CHRM2.C00    13/08/31  21:50:26

** 定量計算結果 **
CH PKNO    TIME        AREA     HEIGHT   MK  IDNO      CONC           NAME
2    24    1.933     7451041   1121644   SVE            62.3557
     27    2.375     3793528   1121381    VE            31.747
     47    4.32         7266      1534   TV              0.0608
     73    6.475       57523     23875   T               0.4814
     75    6.686      221550     93476   V               1.8541
     87    8.007      397880     96936   V               3.3298
     99    8.969       20463      6947   V               0.1712
                   ----------  ---------           ------------
          TOTAL     11949248   2465791                 100
```

GC-1700 (Shimadzu), FID
Inertcap 17 (ID 0.25 mm, L 30 m, df 0.25 μm)

Program: 100 °C → 250 °C, 10 K/min
Inj : 300 °C, Det : 300 °C, Press of N_2: 100 kPa, Flow of N_2 : 25 ml/min

Fig. S4. GC charts of a) the reaction mixture of chemoselective reduction of **1** using **G_3-C_{16}**-$Rh_5(CO)_{15}$ (Table 1, Entry 1) and b) the reaction mixture of reduction of **1** using **DMAPS**-Rh (Table 1, Entry 3).

References

[1S] S. Stevelmans, J. C. M. van Hest, J. F. G. A. Jansen, D. A. F. J. van Boxtel, E. M. M. de Brabander-van den Berg and E. W. Meijer, *J. Am. Chem. Soc.*, 1996, **118**, 7398.

[2S] P. Chini and S. Martinengo, *Inorg. Chim. Acta.*, 1969, **3**, 315.

[3S] A. Fumagalli, T. F. Koetzle, F. Takusagawa, P. Chini, S. Martinengo and B. T. Heaton, *J. Am. Chem. Soc.*, 1980, **102**, 1740.

[4S] J. L. Kreider and W. T. Ford., *J. Polym. Sci. Part A: Polym. Chem.,* 2001, **39**, 821.

[5S] (a) P. Chini and S. Martinengo, *Inorg. Chim. Acta.*, 1969, **3**, 299; (b) R.T. Weberg and J. R. Norton, *J. Am. Chem. Soc.*, 1990, **112**, 1105; (c) S. Kawi and B. C. Gates, *Inorg. Chem.*, 1994, **33**, 503.

[6S] M. J. Haddadin, R. M. B. Zerdan, M. J. Kurth and J. C. Fettinger, *Org. Lett.*, 2010, **12**, 5502.

[7S] E. Vasilikogiannaki, C. Gryparis, V. Kotzabasaki, M. Stratakis and I. N. Lykakis, *Adv. Synth. Catal.*, 2013, **355**, 907.

[8S] B. H. Kim, Y. M. Jun, Y. R. Choi, D. B. Lee and W. Baik, *Heterocycles*, 1998, **48**, 749.

[9S] SDBS Web: http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Science and Technology, 2014. 01. 07.)

[10S] T Tu, Z. Wang, Z. Liu, X. Feng and Q. Wang, *Green Chem.*, 2012, **14**, 921.

[11S] M. A. H. Ismail, D. A. Abou El Ella, K. A. M. Abouzid and A. H. Mahmoud, *Bio. Med. Chem.*, 2012, **20**, 2455.

[12S] N. Kumar, V. Kumar, U. Sharma, B. Singh and P. K. Verma, P. Kumar, *Green Chem.*, 2012, **14**, 2289.